Novel Electromagnetic - Microreactor Design for Ammonia Synthesis

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Abstract— Microreactor design for ammonia synthesis with electromagnetic (EM) induction is reported. The Y-shape reactor with dimension of 50mm by 120mm has 5 mixing channels. This microreactor was designed using 2D AUTOCAD software. It was fabricated using MAZAK milling machine that operates using a numerical control functionality computer which was interfaced with MASTERCAM software. Aluminum metal plate with 2mm thickness was used as the microreactor. It was milled for 30 minutes with 0.5mm width of the channel. After the milling process was done two inlets and one outlet with pipe connectors were assembled. To reduce the leakage, a gasket paper was placed between the two plates. Hydrogen and nitrogen gas were mixed and flowed (1.2 bar) into the inlet with 0.05g manganese based ferrite used as the nano-catalyst. The reaction was done in ambient condition. The microreactor was placed in a Helmholtz Coils to induced strong EM field. We used Kejldahl method to calculate the 24.9% ammonia yield.

Index Term— Microreactor, micromixer, AUTOCAD, MAZAK, MASTERCAM, ammonia synthesis, nanocatalyst, and Kejldahl method.

I. INTRODUCTION

In plant process the quantity of hazardous chemicals are typically very huge and unsafe and consume high operation energy. Hence, there has been an increased in the study of chemical microreactors to replicate those commonly used in the industry [1]. They have several advantages particularly on the high surface area to volume ratio. Due to their small volume, fast changes of operating conditions can be performed with minimal time demand to reach equilibrium state [2]. On top of this the capability to test a number of catalytic reaction in separate reaction chambers, without any interference by flow mixing would guarantee high accuracy and reliability of the final results [3]. Development of a structured – aluminum – anodized alumina microreactor was done by [4]. It was found that the reactor was able to convert 99% of ammonia to hydrogen. Increased reaction rate at ambient pressure by one order of magnitude, from 0.004 mol gcal−1min−1 in ambient condition to 0.046 mol gcal−1min−1 at 51 bar and 71% was reported [5].

This silicon/glass microreactor was able to handle high pressure and provide optical access into the reaction channel for flow investigation. Different types of microchannel architectures was constructed which at 5°C, full conversion of 6 vol.% of NH3 was obtained. The design was able to produce ammonia conversion as high as 20% with the temperature difference between different reaction channels [6]. A review on microchip multiphase chemistry was also done [7] which concluded that the most difficult multiphase system to develop was gas liquid – solid system. On the other hand the most advanced solid catalysts interaction principle for this system is the fix-bed reactor principles [7]. Development of this technology is recently been approach due to its vast advantages. Several types and unit operations that has been studied namely, micro-heat exchangers, micromixer, microseparators, gas phase reactors, liquid phase reactors of gas –liquid reactors [8].

Microchemical engineering become a significant importance field in chemical engineering. Microreactor is defined as a miniaturized reaction system fabricated using methods of microtechnology [8,9]. The development of this technology is recently been approach since it had come out with a lot of advantages as mini-plant functionality. In microchemical plants, chemical reactions are carried out in three-dimensional structures with inner dimensions in the range of micrometers. The technology of microreactor lead to an enhanced mass and energy transport. An accurate control of relevant process parameters like pressure, temperature, and residence time and flow rate can be easily done by the use of micro chemical plants. The application of micro chemical engineering offers advantages with regard to several factors. A yield improvement of 10-25 per cent and savings of energy costs of 5-15 per cent due to process intensification as well as reduced laboratory and investment costs for continuous processes exert influence on the profitability of the product [9]. The main field of application of micro chemical engineering is the process intensification in the pharmaceutical and fine chemical industry. Thereby significant improvements in product yield.
and quality can be reached. The use of micro chemical methods is particularly reasonable for the performance of reactions involving challenging conditions. Since the recent initiation of micro chemical engineering a large amount of possible reactions for this technology has been presented. It was proven that microreactor can exhibits high catalytic activity at moderate temperatures. Microreactor has been developed based on aluminum body which has disadvantage low melting point (660°C) [4]. In designing a single microreactor, there are things that need to be considered [9]. Those facts are:

- **Microreactor size.**
  Channel design requires accurate methods for prediction of fluid pressure drop studies for various liquids in microscale conduits that are used in the various microreaction technology.

- **Microreactor length scaling**
  To apply the principles of continuum mechanics, critical lengths can be defined for gases and liquids above which continuum theory is valid.

- **Microreactor materials and fabrication method**
  Cost and process application requirements will both dictate the final choice for materials of construction and fabrication technology.

This work was initiated to produce ammonia in electromagnetic (EM) field environment. A Y-shape microreactor was designed and fabricated. Single phase manganese based ferrite which was synthesized using sol-gel method, was used as the nanocatalyst. The yield of ammonia was calculated using Kjeldahl method.

### 1.1 Ammonia synthesis

Ammonia is one of the most highly produced inorganic chemicals and the ammonia produced is mostly used for fertilizing agricultural crops [10]. The synthesis of ammonia in mostly modern ammonia-producing plant is described below:

- Catalytic hydrogenation converts organ sulfur compounds into gaseous hydrogen sulfide:
  \[ \text{H}_2 + \text{RSH} \rightarrow \text{RH} + \text{H}_2\text{S}(g) \]  
  (1)

  The hydrogen sulfide is then removed by passing the gas through beds of zinc oxide where it is absorbed and converted to solid zinc sulfide:
  \[ \text{H}_2\text{S} + \text{ZnO} \rightarrow \text{ZnS} + \text{H}_2\text{O} \]  
  (2)

- Catalytic steam reforming of the sulfur-free feedstock is then used to form hydrogen plus carbon monoxide:
  \[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 2\text{H}_2 \]  
  (3)

- Water gas shift reaction used to convert the carbon monoxide into carbon dioxide and more hydrogen:
  \[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]  
  (4)

  The carbon dioxide is then removed either by absorption in aqueous ethanalamine solutions or by adsorption in pressure swing adsorbers (PSA) using proprietary solid adsorption media.

The final step in producing the hydrogen is to use catalytic methanation to remove any small residual amounts of carbon monoxide or carbon dioxide from the hydrogen:

\[ \text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \]  
(5)

\[ \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \]  
(6)

Ammonia synthesis loop (Haber – Bosch process):

\[ 3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3 \]  
(7)

### II. METHODOLOGY

#### 2.1 Microreactor Design

The drawing of the design was produced using the 2D AUTOCAD software. Estimation on how far or how long the mass transfer has occurred in diffusion controlled systems, the principle below were used:

\[ \frac{d^2 l}{d t^2} = \frac{d^2 Y}{d l^2} \sim 1 \]  
(8)

where, \( l \) is the diffusion length, \( D \) is the diffusion coefficient, \( t \) the time, \( V \) the flow speed and \( L \) is the travelling length.

There is an assumption on the mixing process. The assumption was made under the steady state which were taken by

\[ \nabla \cdot \mathbf{V} = 0, \]

\[ \mathbf{V} \cdot \nabla \mathbf{V} = -\frac{1}{\rho} \nabla P + \mathbf{v} \nabla^2 \mathbf{V}, \]

\[ \mathbf{V} \cdot \nabla \mathbf{C} = D \nabla^2 \mathbf{C}, \]  
(9)

where \( \mathbf{V}, \mathbf{P}, \) and \( \mathbf{C} \) denote the velocity vector, the pressure, and the concentration respectively [10]. The concentration of ammonia produced represents the amount of mixing. The detail design with dimensions of the reactor is shown in Fig. 1. The inlet and outlet use is 5mm diameter where else the catalyst hole is put at 3mm diameter. The reactor consist of 2 layer which it include inner layer and outer layer. The inner layer contains the mixing channel and the outer layer contains the hole for the inlet, outlet and catalyst hole. The size of this reactor is 5mm x 120mm x 2mm. This reactor was fabricated on an aluminum plate.
2.2 Microreactor Fabrication

The technology of milling machine was used for the fabrication of the microreactor. The machine gives an accurate shape of mixing channel since uses computer numerical control for its operation. The requirement of this machine to produce the shape of mixing channel is 2D drawing on AUTOCAD software. The challenge comes when the aluminum plate used was too thin to be clamped for the milling process to be done. So, in order to make it clamped, the plate was tightened on thick plywood by using bolt and nut. This can increase the thickness of the plate for the clampers to hold the plate.

The machine used MAZAK Variaxis 630-5X. MAZAK machine with MASTERCAM software interfaced to the machine. In MASTERCAM, the 2D’s drawing for the reactor was initialized. All the parameters were set for the machine, namely, the size of the driller that was used, the depth of the milling process, the speed of the driller and the shape of the driller used. This software simulated the milling process before it generates code for the machine to run. Fig. 2 shows the steps taken for the milling process.

The fabrication was done perfectly and the reactor was assembled with its outer layer as shown in Fig. 3 (a). The inner layer then had been cut according to the design. The two layers of the microreactor were then combined. To combine both of these layers the gasket paper was used.

Fig. 1. Drawing of the reactor using the 2 D AUTOCAD with their dimension. The dimension is in millimeter. (a) The dimensions of the mixing channel. (b) The dimension of first layer of the aluminum plate with the mixing channel on it. (c) The dimension of the outer layer with the hole of inlet, outlet and the catalyst hole.

Fig. 2. The parameter setting and simulation for milling process in MASTERCAM software. The simulation takes 30 minutes to complete.

Fig. 3. (a) The components for the reactor. The mixing channel is produced on inner layer. (b) The assembling of the reactor. To tighten the reactor, bolt and nut been used. Pipe connectors were used as the inlet and outlet connections.
2.3 Helmholtz Coil
A Helmholtz Coil consists of two identical circular magnetic coils that were placed symmetrically one on each side of the experimental area along a common axis. The microreactor was placed in the middle of the two identical circular magnetic coils by clamping it to a retort stand (Fig. 4). In this experiment we used 0.55 A and 3.8 V to drive the 320 n turns Helmholtz Coil with strong electromagnetic waves. Fig. 4 shows the schematic diagram of Helmholtz coil.

Fig. 4. (a) Helmholtz Coil and the microreactor connected. (b) Helmholtz Coil/ microreactor with the Power Supply

2.4 Catalyst Preparation
Manganese-based ferrite (MnFe₂O₄) was introduced as a new catalyst for ammonia synthesis. It was synthesized by using sol gel method [11]. The as-prepared sample consists of 99% purity of manganese nitrate (Mn(NO₃)₂.6H₂O), zinc nitrate (Zn(NO₃)₂.9H₂O) and iron nitrate (Fe(NO₃)₃.9H₂O). All of the precursors were dissolved in 65% of nitric acid and stirred for 3 days to get the homogeneous solution. The mixture was then heating at 70°C until the gelatine was formed. After that the sample was dried in an oven at 110°C. The green powder was then crushed for 2 hours and annealed at 700°C in argon environment for 4 hours. We used multiwall carbon nanotubes as a support.

III. RESULTS AND DISCUSSIONS
Ammonia has been produced by using our new microreactor and nanocatalyst (manganese ferrite). Ammonia was formed at room temperature (28°C) and ambient pressure. By using EM field, the electrons were aligned and the catalytic activity took place. Instead of the heat energy in pressurized environment, the activity took place due to the strong exchange interaction between the nitrogen and hydrogen gas with the catalysts. We speculate the electron alignment via spin waves of the ferries by placing the microreactor between the Helmholtz coils has initiated the catalytic activity (Fig. 5).

The method to trace the ammonia is by titration method named Kjeldahl method [12,13].

\[
\begin{align*}
\text{HCl}_{\text{reaction}} & + \text{NH}_3 \rightarrow \text{NH}_4\text{Cl} \\
\text{NaOH} & + \text{HCl}_{\text{excess}} \rightarrow \text{NaCl} + \text{H}_2\text{O} \\
\text{HCl}_{\text{total}} & = \text{HCl}_{\text{reacted}} + \text{HCl}_{\text{excess}}
\end{align*}
\]

\[
\begin{align*}
\text{HCl}_{\text{total}} & = 2.5 \text{ ml} \\
\text{Mole } \text{HCl}_{\text{total}} & = \frac{2.5 \times 0.01M}{1000} = 2.5 \times 10^{-5} \\
\text{Amount of HCl}_{\text{reacted}} & = \text{Amount of NH}_3 \\
\text{Amount of HCl}_{\text{excess}} & = \text{Amount of NaOH} \\
\text{MnFe}_2\text{O}_4 \text{ as nanocatalyst}
\end{align*}
\]

\[
\begin{align*}
\text{HCl}_{\text{excess}} & = \text{NaOH} \\
& = 1.88 \text{ ml} \\
& = \frac{1.88 \times 0.01M}{1000} = 1.88 \times 10^{-5} \text{ mole} \\
\text{HCl}_{\text{reacted}} & = \text{NH}_3 \\
& = (2.5 \times 10^{-5}) - (1.88 \times 10^{-5}) \\
& = 0.62 \times 10^{-5} \text{ mole} \\
\text{Mole fraction of NH}_3 & = \frac{0.62 \times 10^{-5}}{2.5 \times 10^{-5}} \times 100\% \\
& = 24.8 \%
\end{align*}
\]

Ammonia synthesis was done by diluting the gas in to 2.5ml of 0.01M HCl which produced NH₄Cl. After that the titration process was done by using 0.01M NaOH. The amount of NH₃ produced is equal to the amount of HCl_{reacted}. The Mn based ferrite 24.9% ammonia yield. The second experiment conducted using using Mn based ferrite with multi wall carbon nanotubes (MWCNT’s) as the support. The result (Fig. 6) shows that by using MWCNT’s as a support, the yield was decreased 51.8% (Fig. 6). It should also be noted that we used less catalyst (by 50%)
IV. CONCLUSION

Ammonia gas was produce by using our Y-shape microreactor designed in-house. It was speculated that the EM field was able to induce magnetic alignment to the Mn based ferrite catalyst. This had resulted to high ammonia yield 24.9% in ambient conditions.

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REFERENCES


